Chapter 7

Conclusions

7.1 Concluding Remarks

The study of cerium based Kondo systems has achieved a lot of significance due to the wide variety of physical phenomena these compounds exhibit. In the concentrated Kondo systems (CKS), two interactions, viz, the intrasite Kondo interactions and the intersite RKKY interactions compete with each other and the strength of this competition is one vital factor in deciding the type of ground state that such a compound will possess. These two interactions work in opposite direction, but are mainly dependent on the strength of hybridization between 4f level and the conduction electrons. The hybridization depends mainly on two mechanisms: electronic concentration variation and the volume reduction of the ligand atom. Both these mechanisms bring about a change from a magnetically ordered ground state to a nonmagnetic ground state in two different ways. The present investigation was undertaken with a view to study and understand the competition between the Kondo and the RKKY interactions in a cerium Kondo system, CeSi$_{2-x}$Ga$_x$. We chose this system because of the large variety of ground states it exhibits. The undoped compound, CeSi$_2$ with tetragonal structure is a nonmagnetic, Kondo lattice system. Ferromagnetic order sets in with Ga doping at Si site. The magnetic order is preceded by abrupt increase in Ce-Ce bond distance which localizes the 4f level strengthening the RKKY interactions. In the region, $0.7 \leq x \leq 1.3$ ferromagnetic ordering temperature decreases with increasing $x$ but the cell volume remains almost constant. It may be noted here that Si and Ga both have a different outer electronic configuration which will also affect the k-f hybridization. We have studied three compositions from this region, viz, $x = 0.7, 1.0$ and $1.3$. Further increase in Ga concentration leads to a structural transformation from tetragonal to hexagonal structure, similar to that of CeGa$_2$. This structural transformation is also accompanied by magnetic transformation from ferromagnetic to antiferromagnetic at around $x = 1.5$. The compound CeGa$_2$ itself has more than one magnetic transition, last one being ferromagnetic at 8.7 K. We have studied three compositions from this side of the series, $x = 1.4, 1.5$ and $1.75$ along with CeGa$_2$. In this concentration range there is of course the electronic concentration effect...
as well as there is a change in the cell volume. These compounds were characterized by
different techniques such as magnetization, heat capacity, inelastic neutron scattering and
resistivity. The main objectives here were:

- to compare and correlate the results obtained from this different techniques and get a
  consolidated view on the competition between the two processes in this system,

- to study the effect of crystalline electric field on the ground state properties of this
  system and

- to calculate the transport properties form the neutron scattering linewidths treating
  them in a phenomenological model.

In Chapter 1, 2 and 3, respectively, an introduction to cerium based Kondo systems,
basic concepts of inelastic neutron scattering and a brief description of various experimental
 techniques used in this thesis is presented.

In Chapter 4 we describe the magnetic and heat capacity measurements carried out on
these systems. Except for \( x = 1.4 \) sample, on all other compositions susceptibility and heat
capacity measurements have been performed earlier by other workers. Our measurements
are in good agreement with them. We have measured magnetization as a function of tem-
perature at various fields of 100Oe, 2KOe and 10 KOe. The susceptibility curves indicate
that in all the six compositions Ce is in 3+ state and has a good magnetic moment. The
paramagnetic Curie temperatures \( \theta_p \) are negative for compounds ordering ferromagnetically
and negative but small for those ordering antiferromagnetically. We have also carried out
hysteresis measurements in fields of \( \pm 5 \) Tesla at 5K in all the three tetragonal systems.
These measurements indicate that short range magnetic correlations are present in these
systems. These magnetic correlations weaken with increasing Ga concentration. This is
mainly due to the difference in the outer electronic configuration of Ga with respect to Si
which causes a change in hybridization between the 4f level and the conduction band. In
case of the hexagonal systems, \( x = 1.4 \) compound orders ferromagnetically with weak short
range magnetic correlations. The paramagnetic Curie temperature is also negative in this
case. Further increase in Ga concentration changes the magnetic order to antiferromagnetic
type with 0 or negative \( \theta_p \). The change in magnetic order is probably due to change in sign
of the term \( \sum_i 2k_F R_i \).

The heat capacity (C) measurements also confirm the value of magnetic ordering tem-
perature derived from the magnetization measurements by way a of a Schottky anomaly in
the C versus T curves. In the tetragonal compounds appreciable decrease in intensity in the
jump in specific heat at \( T_C \) is seen from \( x = 0.7 \) to \( x = 1.3 \). In case of \( x = 0.7 \) a sharp transi-
tion at \( T_C \) indicates dominance of magnetic interactions in this compound. The decrease
in intensity can then be attributed to the increasing k-f hybridization with increasing Ga
concentration. The intensity distribution can be well accounted for by the \( S = 1/2 \) resonant
model in the tetragonal compounds. In case of hexagonal compounds practically no change
in intensity is seen in all the doped compounds. A possible explanation to this can be given taking into account both, the electronic concentration effect and the volume effect. In the hexagonal systems, as mentioned above, both the effects are present but they act in opposite direction. And the decrease in the magnetic ordering temperature is then probably due to dominance of volume effect over the other effect. The support to this also comes from the fact that the magnetic moment of Ce remains almost constant.

Inelastic neutron scattering is perhaps one of the best techniques to study the ground state phenomena in such systems. The residual quasielastic linewidth gives an estimate of Kondo temperature while the nature of hybridization can be understood on the basis of its thermal evolution. The crystal field (CF) splitting of the ground state is also directly observable with this technique. There are some difficulties in this technique regarding the sample size and subtraction of phonon background from the experimental data. One should be very careful in handling the latter problem as improper phonon subtraction can lead to erroneous conclusions. Since such an experiment was being done for the first time in Trombay, we thought it was worthwhile to first study a well characterized system so that we could compare our results with those reported in literature rather than starting from a new system straightaway. The compound, CeSn₂In, was studied under this context. The results of this study are presented in Chapter 5.

The second section of this Chapter presents our study of inelastic neutron spectra of CeSi₂₋ₓGaₓ. We had to restrict ourselves only to tetragonal compounds due to resolution constraints of the spectrometer. In these compounds we have studied both the thermal evolution of the quasielastic line width as well as crystalline electric field splitting of the ground state in the temperature interval of 10K to 100K. The thermal evolution of quasielastic linewidth indicates a crossover from a RKKY dominated ground state to a ground state dominated by Kondo interactions. Using an approximation of Coqblin-Schrieffer model one can conclude that this crossover is due to increasing k-f hybridization with increasing Ga concentration. The increase in hybridization is perhaps due to the fact that Ga being an acceptor with respect to Si reduces the band electronic concentration which in effect moves the 4f level closer to the Fermi level.

The main objective of CF analysis was to calculate the CF parameters (Bₗⁿ's) in the CF Hamiltonian. In case of tetragonal symmetry the Ce J = 5/2 ground state splits either in three doublets or a doublet and a quasiquartet. In our analysis we have expressed the CF parameters in terms of coefficients of the eigenfunctions (η) and the eigenvalues (Δᵢ) of the Hamiltonian. The eigenvalues being obtained directly from the experiment leaves only one parameter to be determined by fitting the experimental data to the scattering law for CF case. The parameters so obtained were then used to calculate the DC susceptibility which was compared with the measured DC susceptibility treated in mean field approximation. Our results indicate that for x = 1.0 and 1.3 the 5/2 state of the Ce³⁺ ion is split into three doublets. In case of x = 0.7 only one peak is visible with a large width. We feel that in this compound also the ground state may be split into three doublets which cannot
be distinguished on the triple axis spectrometer at Dhruva. The broadening of the CF peaks with increasing Ga concentration suggests that the hybridization between the silicon p electrons, which are responsible for the CF potential, increases with 4f electrons. This indirectly supports our predicted crossover from a RKKY type Ce compound to a dense ferromagnetic Kondo compound in this series.

Inelastic neutron scattering studies on the hexagonal compounds could not be taken up mainly due to resolution constraints of the spectrometer.

The resistivity measurements presented in Chapter 6 also confirm the above mentioned crossover from a RKKY dominated compounds to compounds wherein Kondo interactions dominate. We have used the phenomenological model proposed by Garde and Ray to calculate the resistivity curves from our neutron scattering linewidths. Here we have pointed out at an important deficiency of this model regarding the motion of the 4f level with respect to Fermi level. From these calculations it can be seen that 4f level in case of $x = 0.7$ compound moves in a very narrow energy range as is expected for a RKKY type of compound in which the 4f level is essentially localized. For the other two compounds, $x = 1.0$ and 1.3, which are Kondo systems and hence the 4f level should have a degree of itenerancy and a temperature dependent motion in the atom as seen from our analysis also.

Thus in case of tetragonal systems all our studies confirm that there is a crossover in CeSi$_{2-x}$Ga$_x$, $0.7 \leq x \leq 1.3$, due to increasing hybridization between the 4f electrons and the conduction electrons as we substitute Si by Ga.

In the case of hexagonal compounds the resistivity measurements do not reveal much information which, we feel is due to the CF splitting of the cerium ground state. The CF splitting in all the three doped samples studied here seems to be pretty much the same. The heat capacity studies, as discussed above, also support this view.

### 7.2 Suggestions for Future Work

Inspite of the large amount of experimental and theoretical work going on on the 'Concentrated Kondo Systems', the type of mechanism(s) responsible for the exotic low temperature properties is far from being understood completely. In the present system studied by us, considering that only two mechanisms, volume reduction and changes in electronic concentration, are responsible for the demagnetization in both the tetragonal and hexagonal compounds and in case of hexagonal systems these two mechanisms work in opposite direction, it still remains to be understood which one of the two reduces magnetic ordering temperature. For this inelastic neutron scattering work at low temperatures on a high resolution spectrometer and single crystal studies will be of very much help. The inelastic neutron experiments are presently being planned and will be taken up shortly as a part of IUC-DAEF project at BARC. The recent papers on high energy spectroscopy like valence band photoemission spectroscopy, bremsstrahlung isochromat spectroscopy, XANES spectroscopy have generated a
lot of interest in these compounds. Especially the conclusive evidence of correlation between Kondo temperature and photoemission spectral function needs to be exploited. This will definitely confirm our findings on the crossover phenomena and the temperature dependent movement of the 4f level in case of compounds in the concentration range $0.7 \leq x \leq 1.3$. The XANES spectroscopy is still considered as one of the most unambiguous techniques to calculate the occupancy of the 4f level in such compounds. Lot of theoretical models have been proposed which exactly replicate the spectral shapes of $L_{III}$ edges of Ce. From a rigorous calculations of the $L_{III}$ edge spectra of a series of compounds one can study different interactions like f-f interaction, k-f interaction and their dependence on the macroscopic properties like Kondo temperature, magnetic ordering temperature etc. XANES features in such compounds have also been used to calculate the interatomic distances. The variation of these distances over a concentration range may shed some light on the type of hybridization mechanism involved.

The main difficulty in Ce systems is that almost every new system exhibits some novel feature of its own. Hence it is absolutely necessary to study every system in detail with as many techniques as possible and then correlate the findings from all these techniques and get a conclusive picture on the Physics of such systems. Such an approach may perhaps help theoreticians to check their formalisms on a number of systems and thereby bring out 'the theory' that has answers to all questions that have been bothering researchers working in this field.